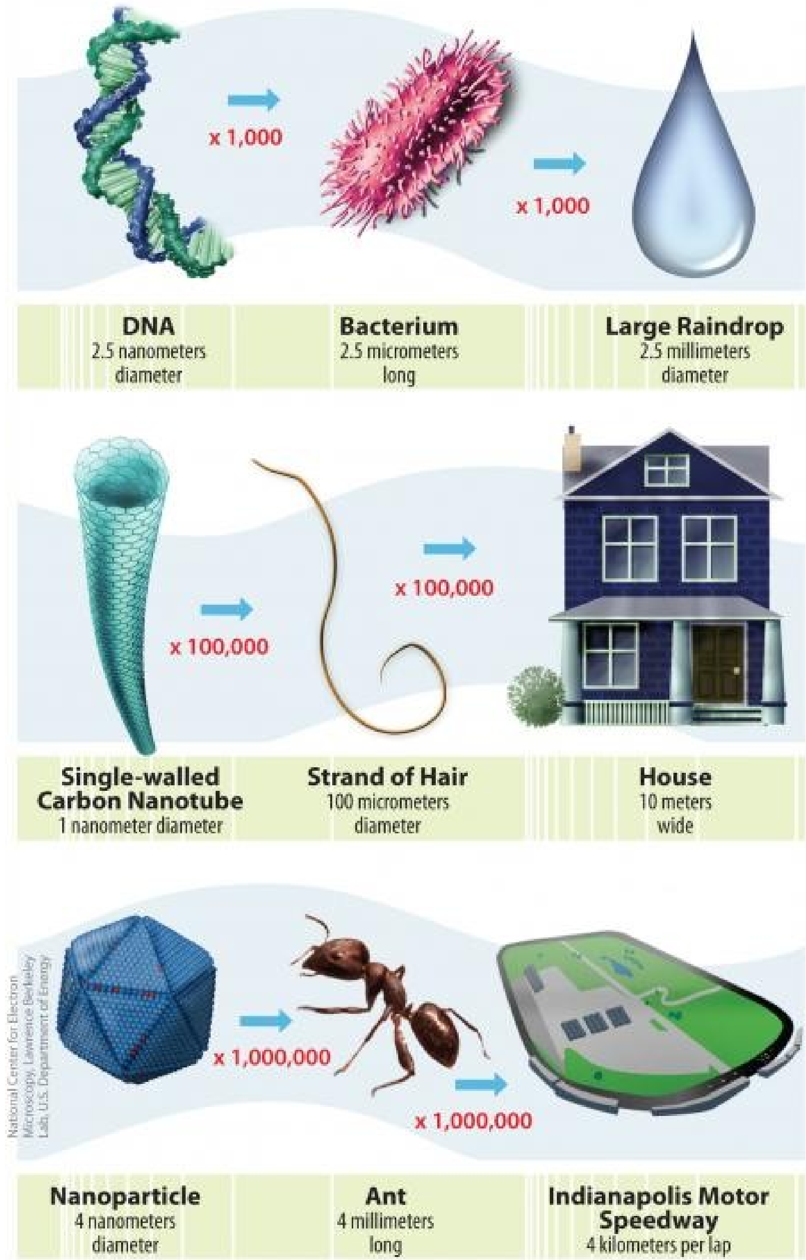
What is Nanotechnology?

- Nanotechnology is a new and broad study of science, engineering and technology conducted in **nanoscale**.
- Nanoscale refers to about **1 to 100 nanometers (nm)**, with 1 nm equals to 1×10^{-9} m.
- A strand of human DNA is about 2.5 nanometers in diameter.
- Nanotechnology is more than just mixing nanoscale



Adopted from: http://www.nano.gov/nanotech-101/what/nano-size

erences between Nano & Bulk Materials

□ **Increased relative surface area**

□ Can change or increase the chemical reactivity.

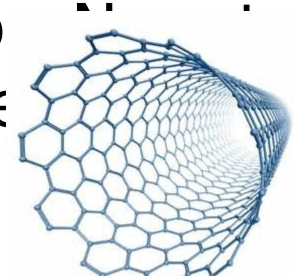
□ **Quantum effect** (□□□□)

□ Can affect material optical, magnetic and electrical properties.

- For example, elemental carbon is a poor conductor of electricity.

  □ Graphene has high charge carrier mobility.

- Another example, Carbo N bes ha ical strength 100 times highe eel (□



Vs

neral Classification of Nanomaterials

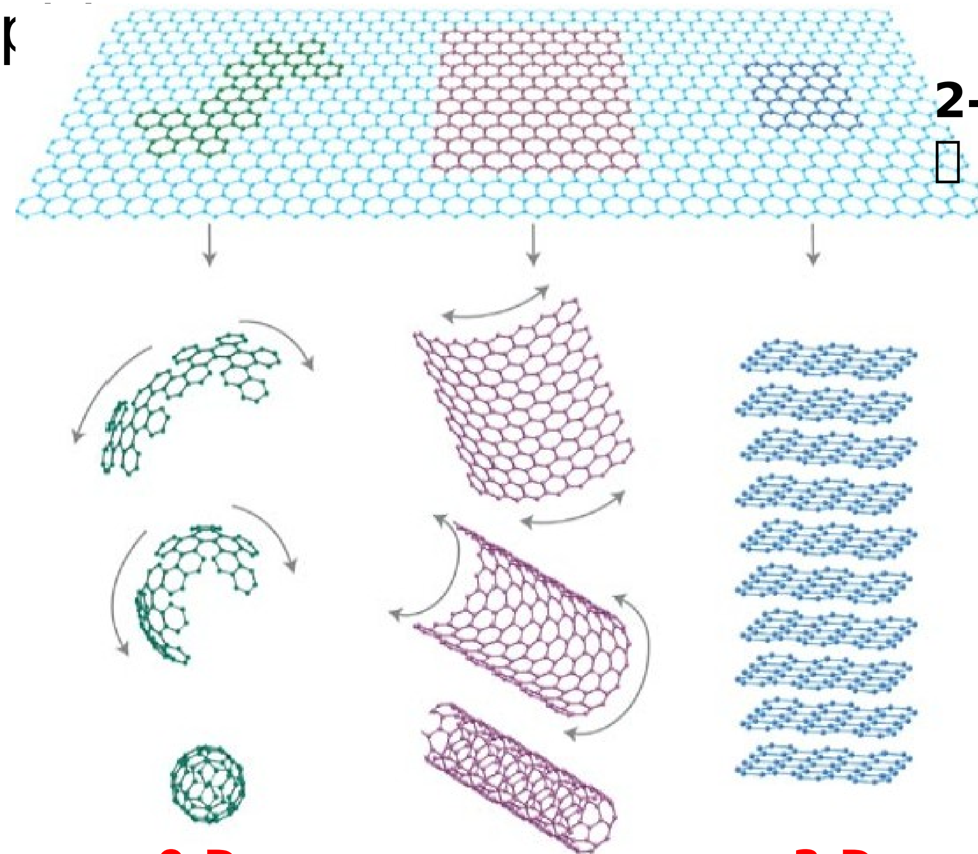
- Nanomaterials can be classified into two different ways, **dimension** and **composition**.

Nanomaterials		
Dimension		
0 – D	**1 – D**	**2 – D**
• Nanocrystals • Buckminsterfullere ne	• Carbon nanotubes • Nanofibers • Nanowires	• Graphene

Nanomaterials			
Composition			
Dendrimers	**Composites**	**Metal-based Nanomaterials**	**Carbon Nanostructures**
• Low molecular weight - Dendrimers - Dendrons • High molecular weight	• Matrix type - Ceramic composite - Polymer composite - Metal	• Metal colloids • Metal oxides • Quantum dots	• Fullerenes • Carbon nanotubes • Graphene

neral Classification of Nanomaterials

- In terms of **dimension**:
- 2-D building material can be wrapped up into 0-D bulkyballs, rolled into 1-D nanotubes or stacked into 3-D grap



2-D building material
Graphene

0-D Bulkyball

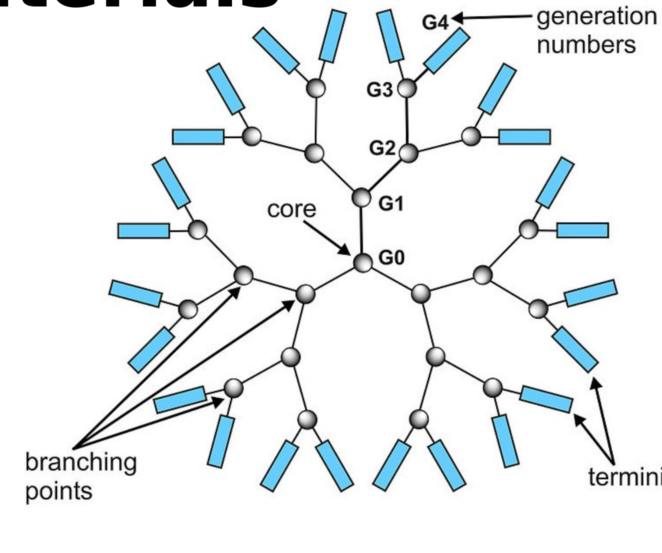
1-D Nanotube

3-D Graphite

neral Classification of Nanomaterials

- In terms of **composition**:

- ***Dendrimers*** are synthetic **macromolecules** of nanometer dimensions built from **branched unit extended from common core**, growing in **different generations** and mainly acting as catalysts.

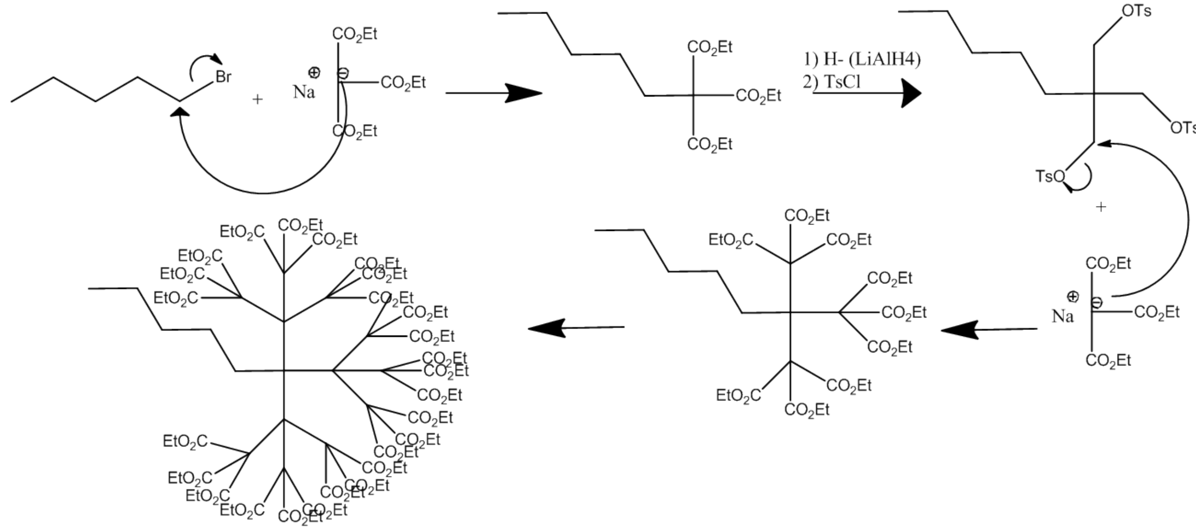


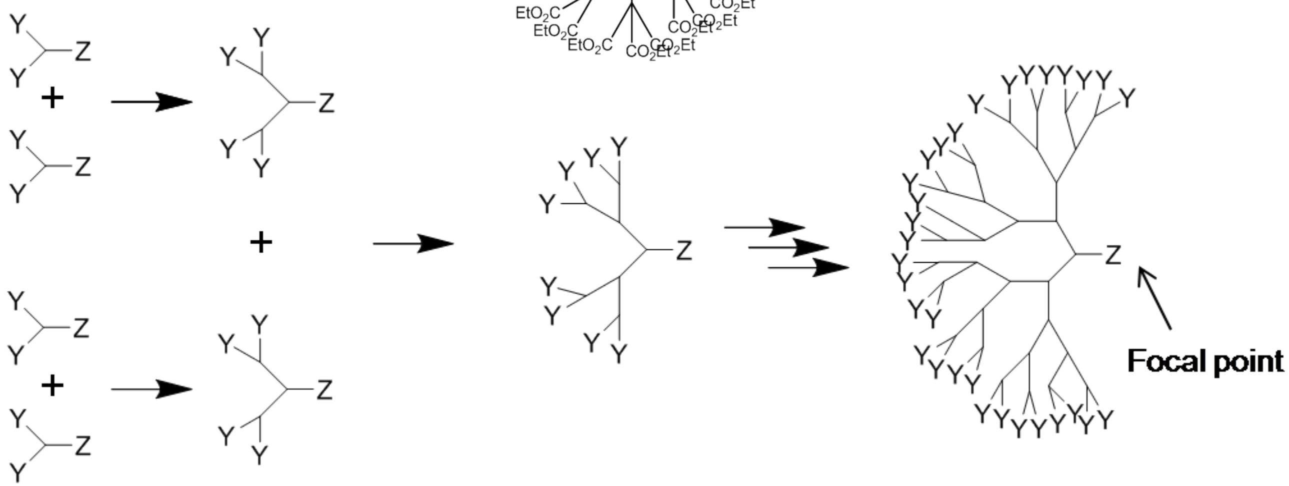
DENDRIMER

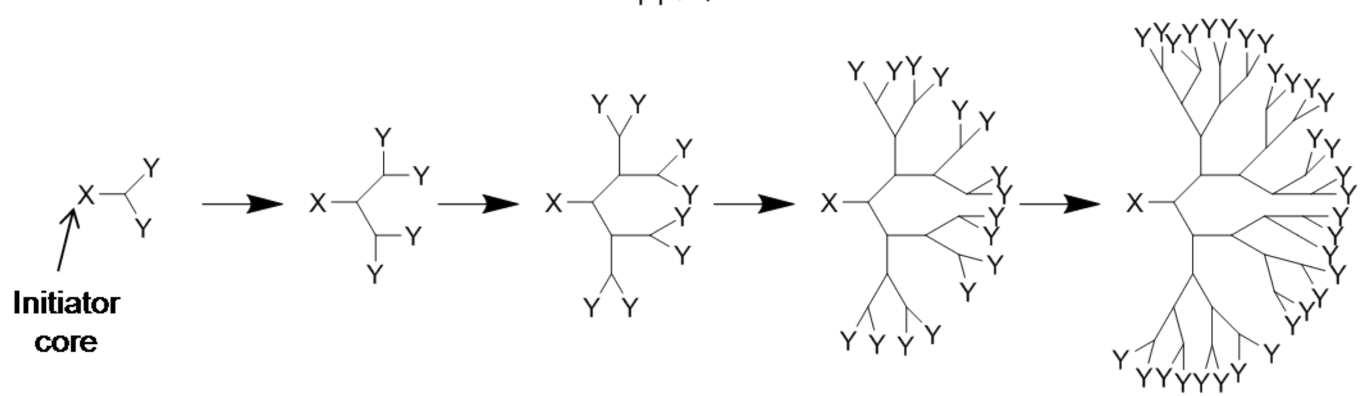
- ***Composites*** are combinations of nanoparticles with other nanoparticles of with larger, bulk-type materials.

- ***Metal-based*** nanomaterials include **metallic and semiconductor nanoparticles** confined (□□) in at least one dimension.

- ***Carbon nanostructures*** are consisted of **carbon**,

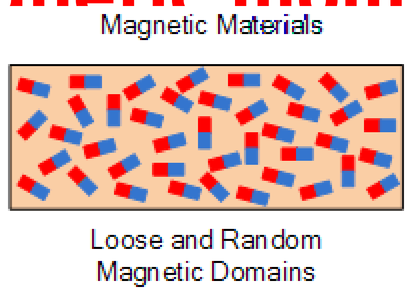

1) H- (LiAlH4)
2) TsCl

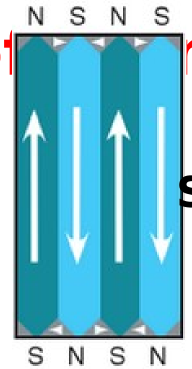

Focal point


Initiator core

gnetic Properties of Nanoparticles

- The source of magnetism in materials is their **constituent atoms**, which consist of **tiny permanent dipolar magnets** whose strength is given by the **magnetic moment of** **m**.





Single Domain formation

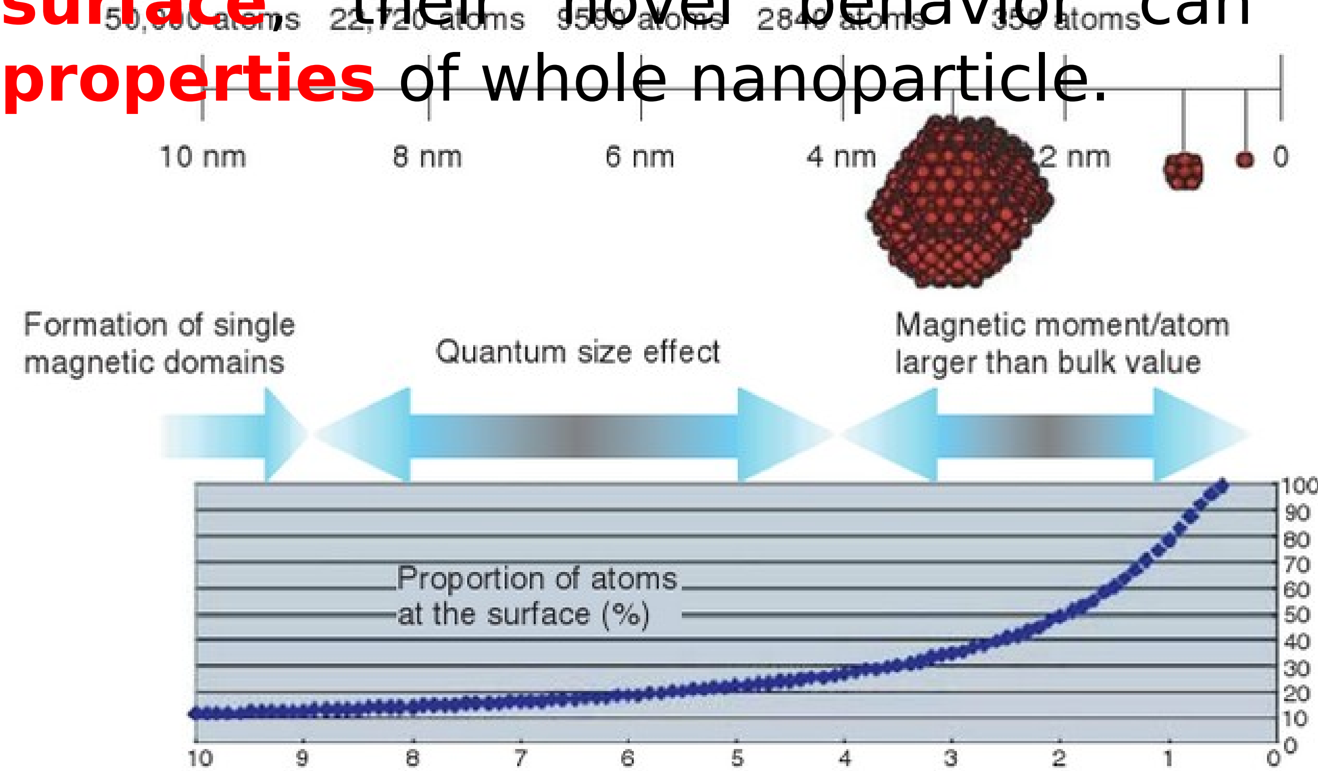
- In **totally magnetized state** of magnetic materials will organize the magnetization into ‘**domain**’ with **opposite alignment** to minimize the energy.

- If the particle is **small enough**, the **strength of its magnetism** (***magnetic moment***) per atom is **increased**

Magnetic Properties of Nanoparticles

- Magnetic moment of a particle depends on the **proportion of atoms that constitute the surface layer**.

- When **high proportion of atoms occupying the surface**, their novel behavior can **distort the properties** of whole nanoparticle.

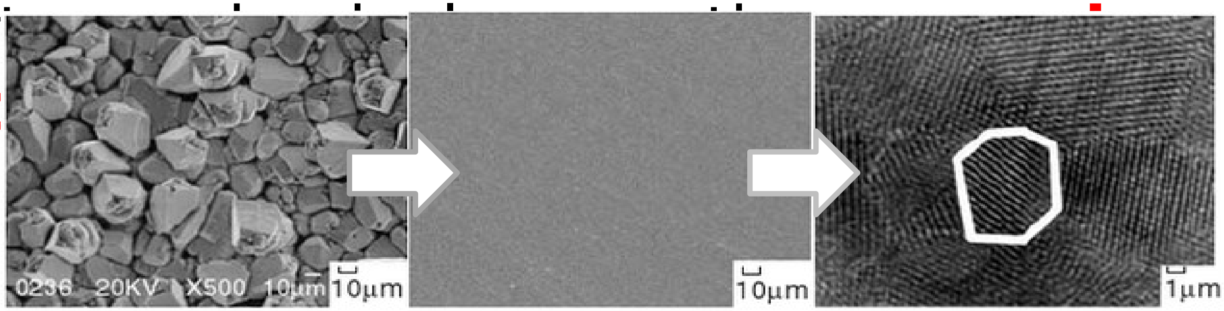


Some original nonmagnetic metals becomes magnetic when they are ***sufficiently small***

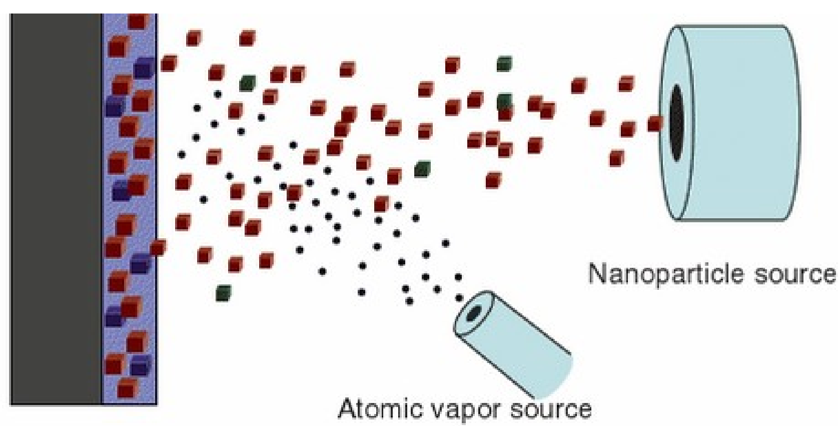
chanical Properties of Nanoparticles

- **Mechanical properties** such as **strength of metals** (how much material ***deforms*** when exposed to a ***force***) can be enhanced by making them with nanoscale grains.

- The **grains boundaries** is important in determining i **slipping each** c



fferent grains sizes



Making granular materials by co-depositing nanoparticles and atoms

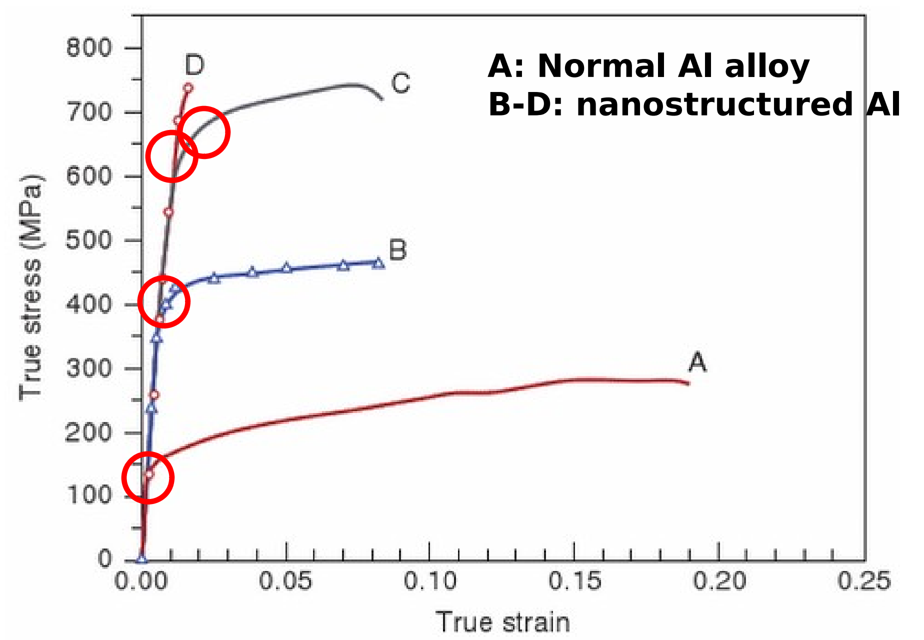
chanical Properties of Nanoparticles

- Nanoparticles have **improved yield strength** (***the load a material can tolerate before it becomes permanently deformed***).

- A plot of strain (relative elongation of sample) versus stress (load) for different nanostructured Al alloy to normal Al alloy.

- Nanostructured materials have a value up to **four times higher** than normal Al alloy.

- The yield strength occurs **slope changes**.

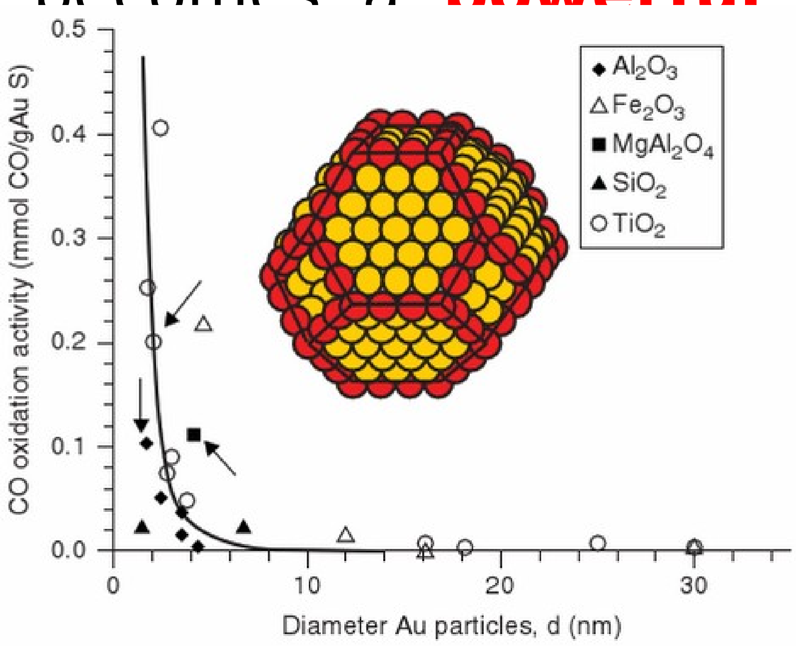


emical Properties of Nanoparticles

- **Chemical reactivity** of nanoparticles mainly depends on □ their **size** and □ **material on which they are supported**.

- When **Gold** is in form of **nanoparticles** with diameter less than 5 nm, it becomes a **powerful catalyst**, especially for oxidat

- Since catalysis occurs at **surface layer of atoms (especially corners – red region)**, size effect dominant.



- This size dominant effect of Gold demonstrates it from a completely inert material to a powerful catalyst.

ewing for the Nanomaterials

- It is impossible to see the materials at nanoscale by our naked eyes.

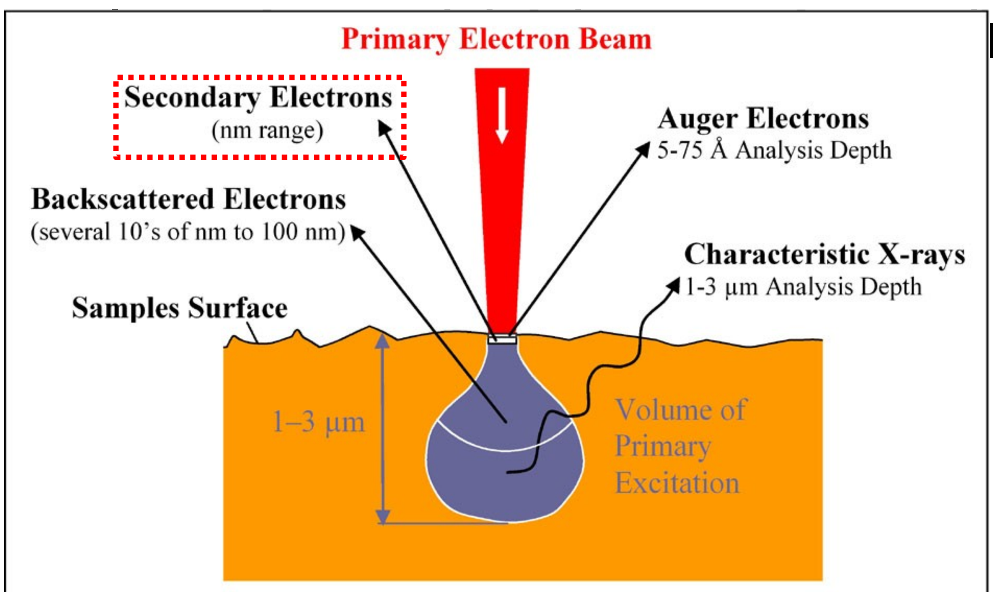
- From 1930s onwards, scientists were able to view the nanoscale using instruments such as **scanning electron microscope (SEM)**.

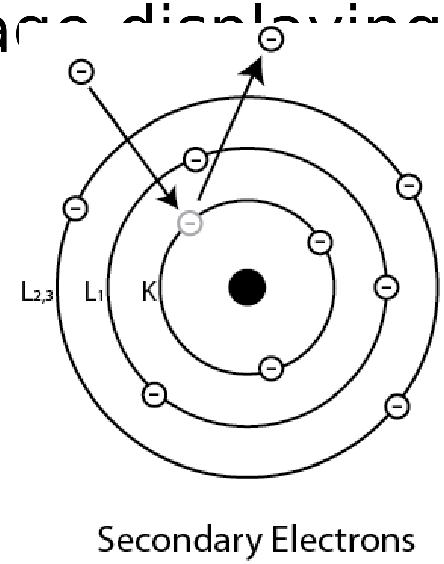
- Until 1980s, the **scanning tunneling microscope (STM)** was developed to view and control nanoscale particles, atoms and small molecules. Its resolution can be as good as 0.1 nm lateral resolution and 0.01 nm depth resolution. STM can be used in vacuum, air, water or other liquid, and temperature from 0 K to few hundred ^{o}C.

- Other instruments such as **atomic force**

nning Electron Microscope (SEM)

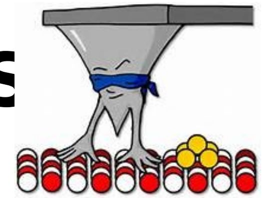
- Images of sample are produced by scanning it with a **focused primary electron beam**.
- The electron has high enough energy to interact with atoms of sample, emitting a **secondary electron** from atom.
- By scanning the sample and collecting secondary ... ma ... **surface**





An inner electron is emitted

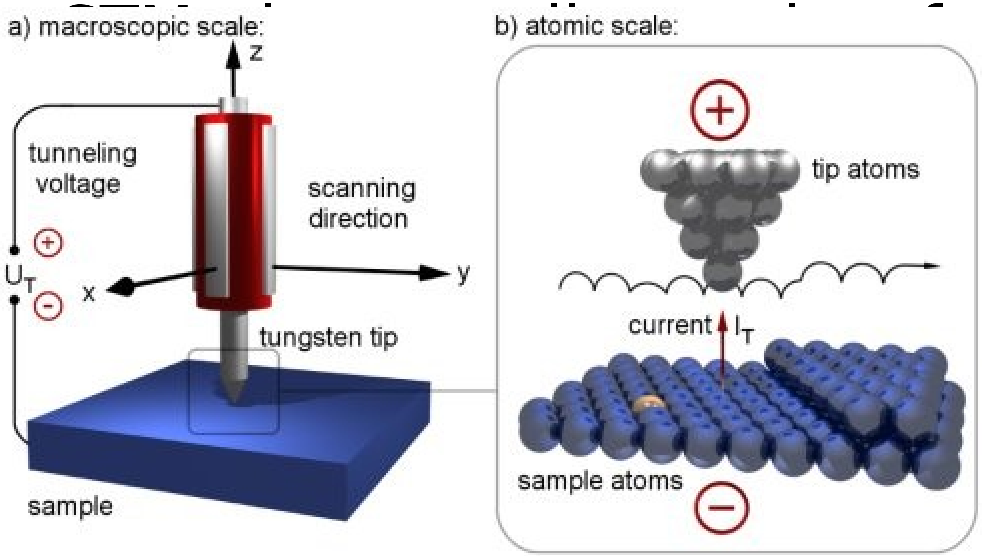
nning Tunneling Microscope (S

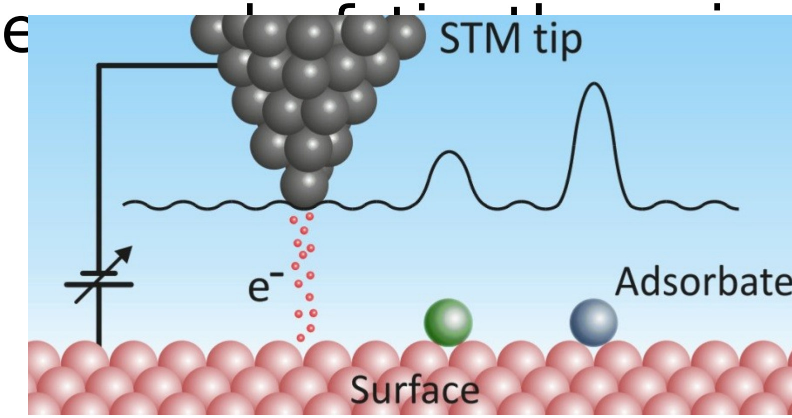


- Based on the concept of **quantum tunneling**. When a **<u>conducting tip</u>** is brought **<u>very near</u>** (few nm) to the sample surface, a voltage difference applied between them can allow **<u>electrons to tunnel through the vacuum between them</u>**. Resulting tunneling current is a function of tip position, applied voltage and sample local density.

tungsten or **platinum-**

ve



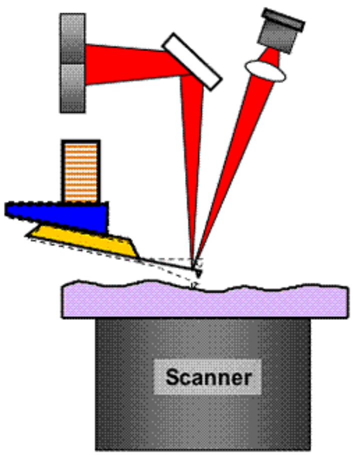


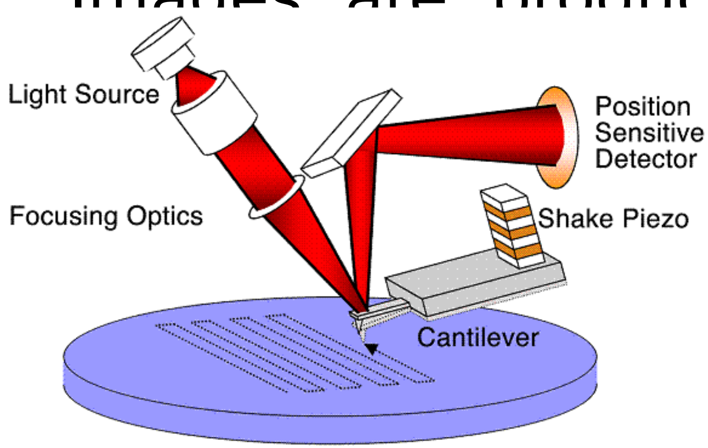
omic Force Microscope (AFM)

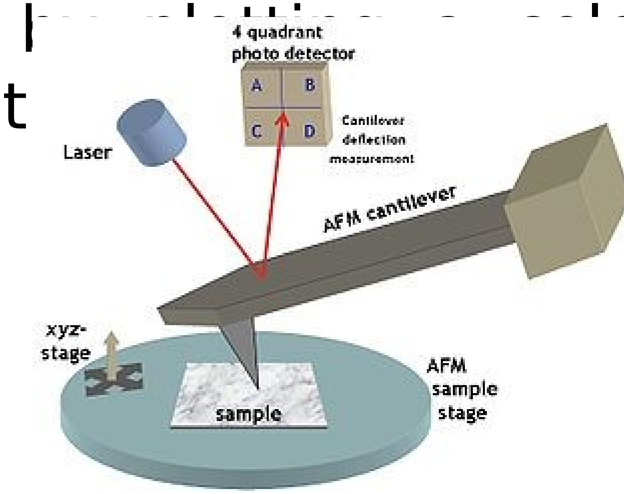
- AFM consists of **cantilever** (□□) with sharp tip at its end to scan the sample surface.

- When the tip is brought to sample surface, **forces** between tip and sample cause a **deflection of cantilever**.

- The deflection is measured by a **laser spot reflected from top surface of cantilever** into a detector. Images are produced b ... or
of t

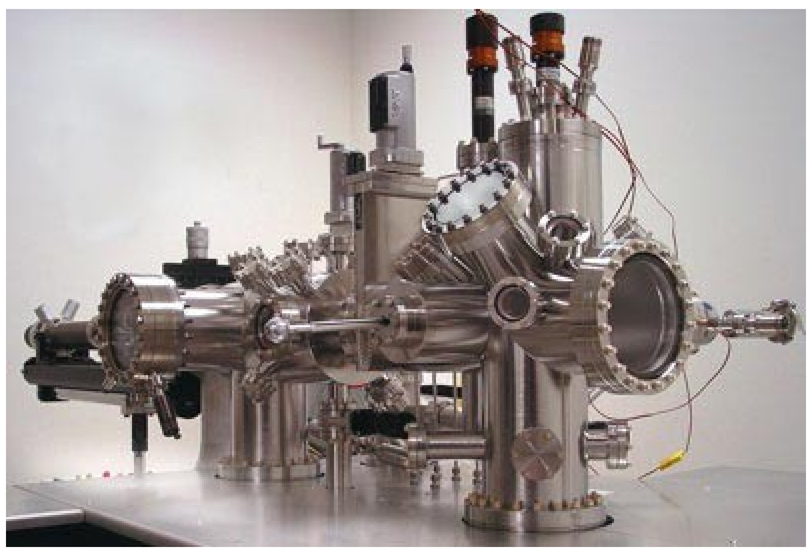




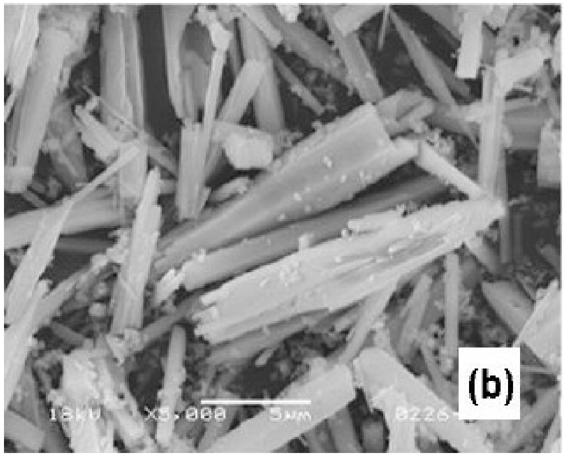


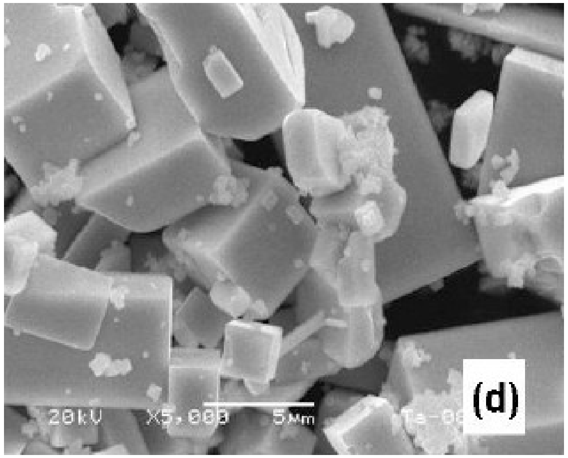
Scanning Electron Microscope (SEM)

Atomic Force Microscope (AFM)



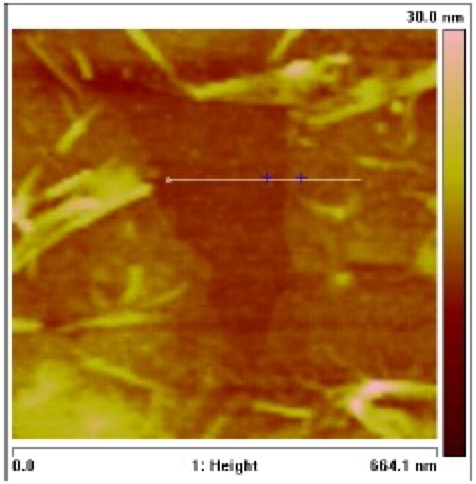
Scanning Tunneling Microscope (STM)





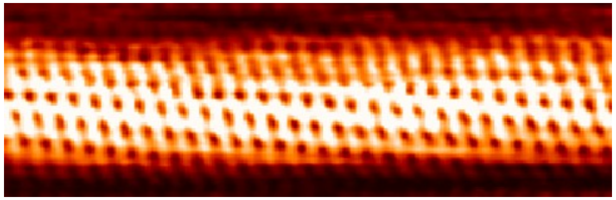
SEM images of some metal-based nanomaterials

Adopted from: Hayashi, H., Hakuta, Y., 2010. Materials (3), 3794-3817.



AFM image of supported graphene film

Adopted from: Lewis M.G.D.A., 2010. University of Southern California.

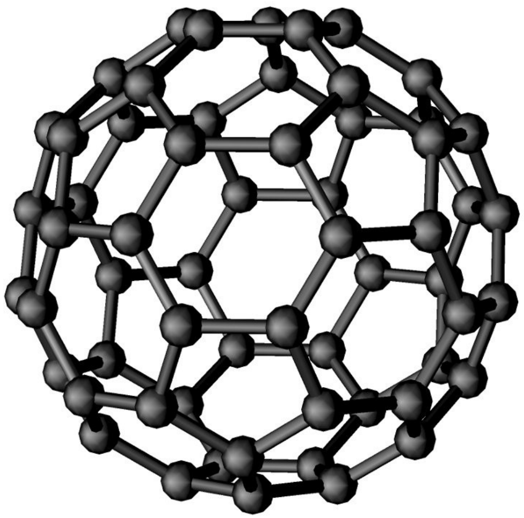


STM image of single-walled carbon nanotube

Adopted from: https://en.wikipedia.org/wiki/Scanning_tunneling_microscope.

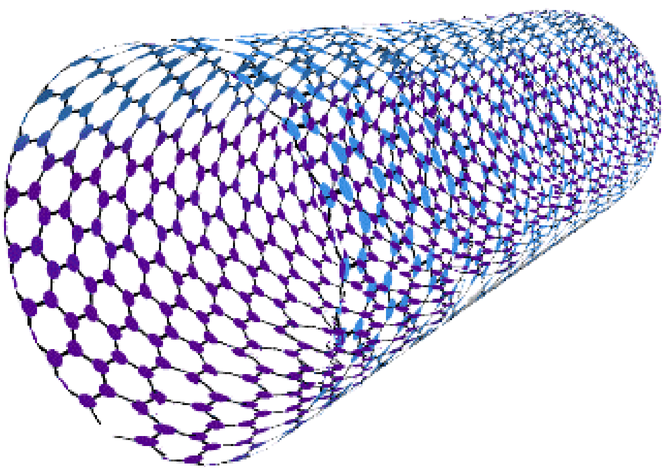
Fullerene

- Fullerenes are the molecule of **Carbon (C)**. The most typical shape are spherical, cylindrical and sometimes other shapes.



Spherical shape

Adopted from: http://isaacs.sourceforge.net/ex.html



Cylindrical shape

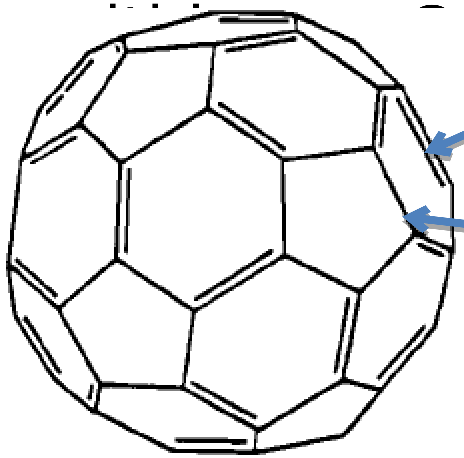
Adopted from: http://www.pcmag.com/encyclopedia/term/47622/nanotube

- Spherical fullerenes are called **buckyballs** while the cylindrical fullerenes are called **carbon nanotubes**

Bulkyballs

- The first fullerene molecules was discovered in 1985, which is called **Buckminsterfullerene C_{60}**.

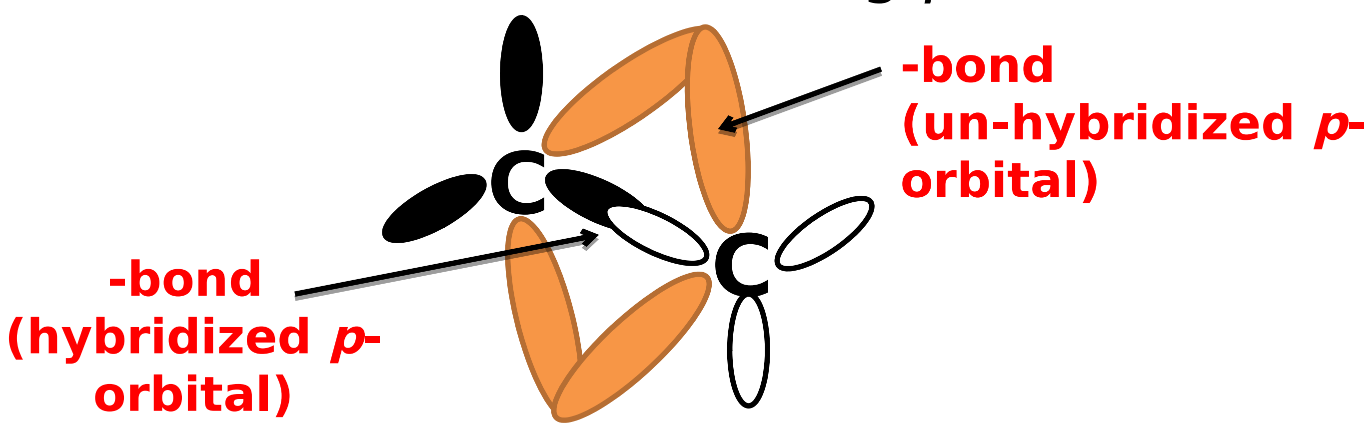
- C_{60} is formed by 60 carbons with **20 regular hexagons** and **12 pentagons**, just like a football. There are 60 **C–C single bonds** and 30 **C=C double bond** $_{0}$ molecule.



- Each carbon is part of one pentagon and two

Bulkyballs

- Each carbon has ***sp***^{2} hybridization, with remaining *p*-orbital available for -bonding. Therefore, each carbon forms **three -bonds** with *sp*^{2} hybridized orbitals and **one -bond** with remaining *p*-orbital.

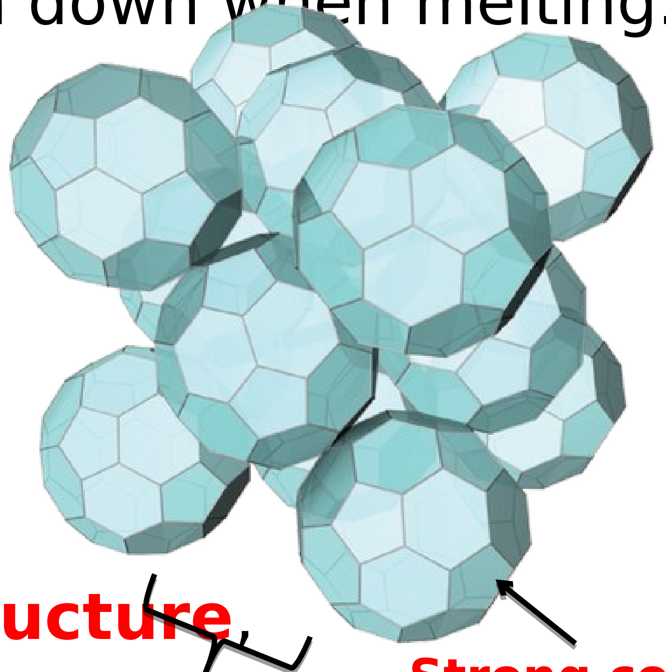


- In C_{60}, the pentagonal rings **prevent the structure from being planar**, making it spherical.

Bulkyballs

- **Within** one C_{60} molecule, the carbon atoms are held by **strong covalent bond**. While **between** each C_{60} molecule, they are held by **weak Van Der Waals' Force**, which has to be broken down when melting.

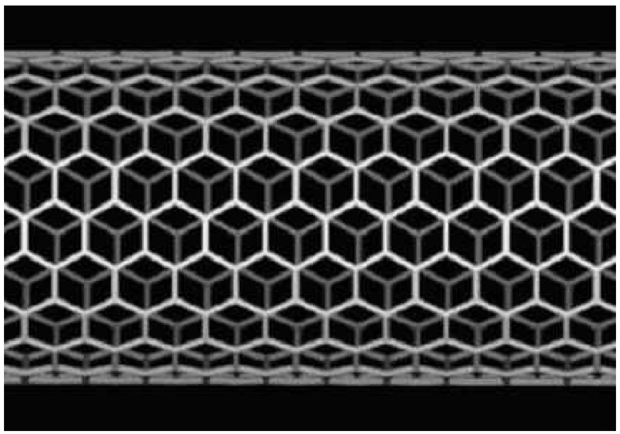
Substance	Melting point (°C)
Graphite	3730
Diamond	3550
Buckminsterfullerene	**1070**



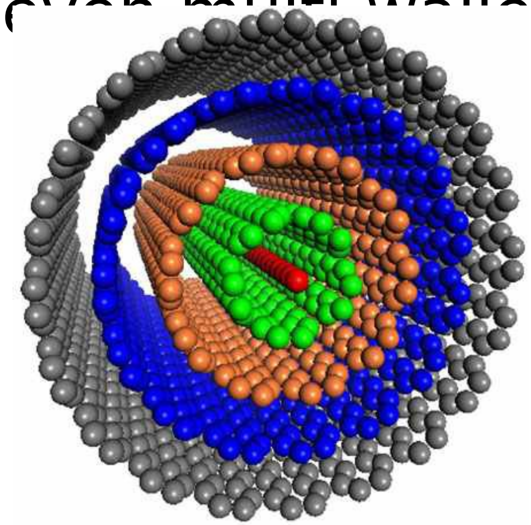
- C_{60} are **simple molecular structure**, their melting points are lower than graphite and diamond.

arbon Nanotube (CNT)

- Carbon nanotubes (CNT) can be single-walled, double-walled, triple-walled or even multi-walled.



Single-walled CNT

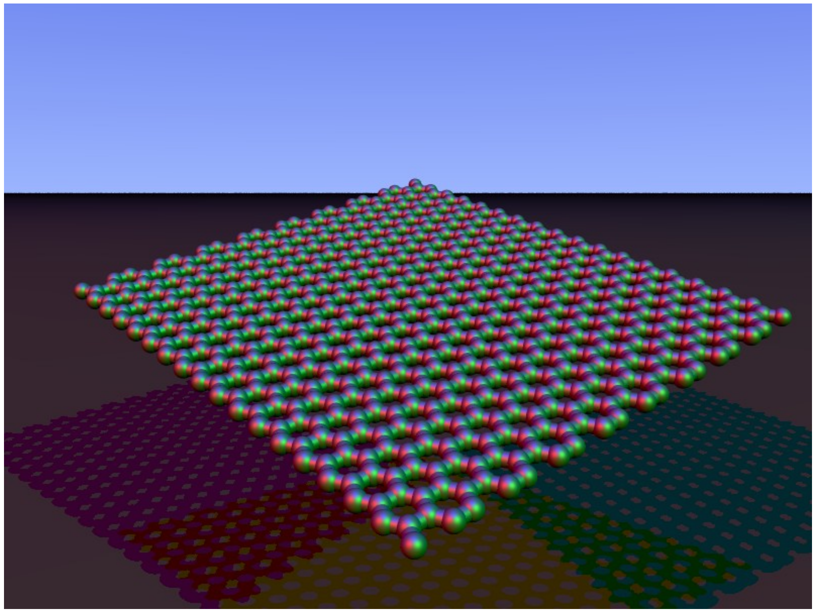


Multi-walled CNT

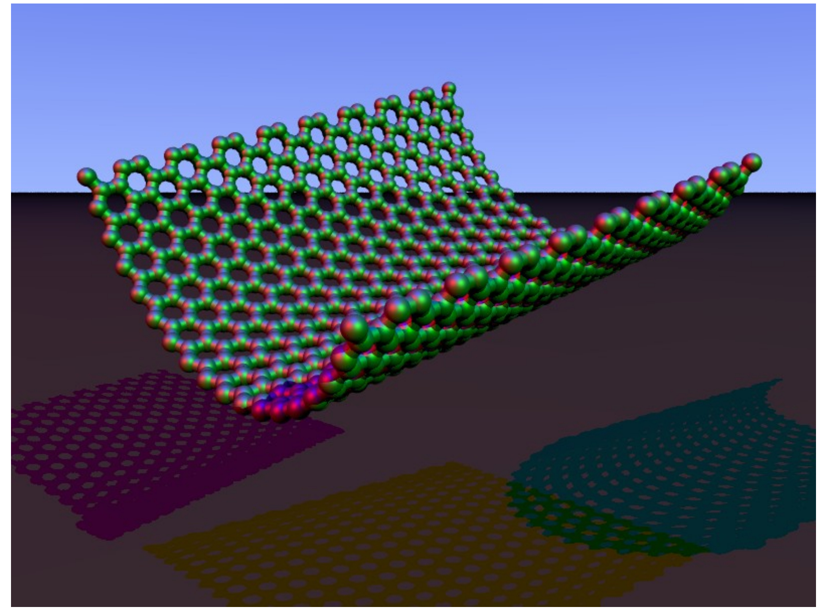
M.D. Nizamul Isla et al., 2011. Carbon nanotube: Implementation of carbon nanotube in supercapacitor. IJEEE. 2231-5284

- **Single-walled carbon nanotube** (**SWCNT**) is formed by rolling up a single layer of graphite – **graphene** into a tube shape.

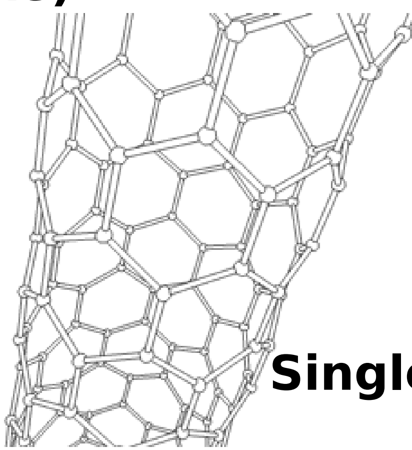
arbon Nanotube (CNT)



A sheet of graphene
(single layer of graphite)



Rolling up a sheet of graphene



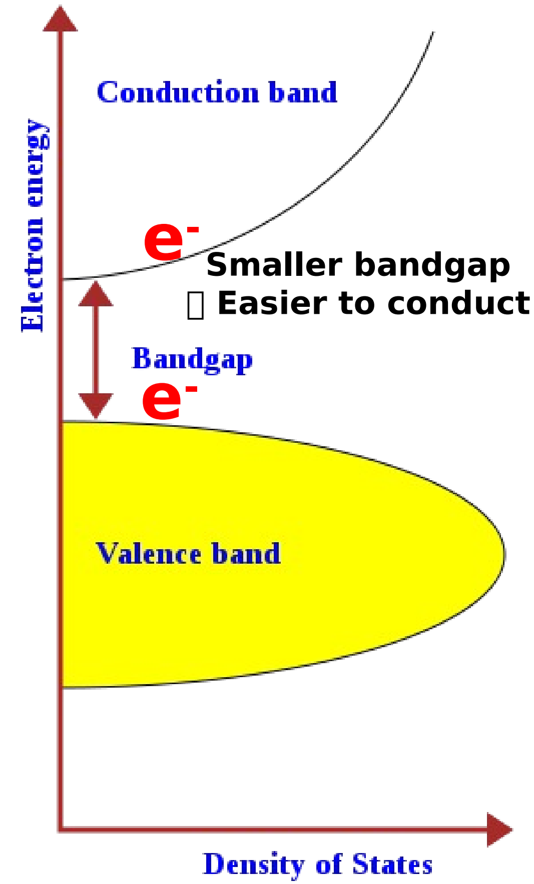
Single-walled CNT

Adopted from:
https://en.wikipedia.org/wiki/Carbon_n
anotube

bon Nanotube (CNT) – Electronic Properties

- **Bandgap** refers to **energy difference** between top of **valence band** and the bottom of **conduction band**.

- **Energy required** to promote valence electron bound to atom to become a conduction electron, which is **free to move** in lattice.



bon Nanotube (CNT) – Mechanical Properties

- CNTs have very **strong mechanical strength** due to the **strong covalent *sp*² bonds** among the carbon atoms.

- Mechanical strength is represented by **tensile strength** (***force per unit area at breaking point***) and **Young's modul s**.

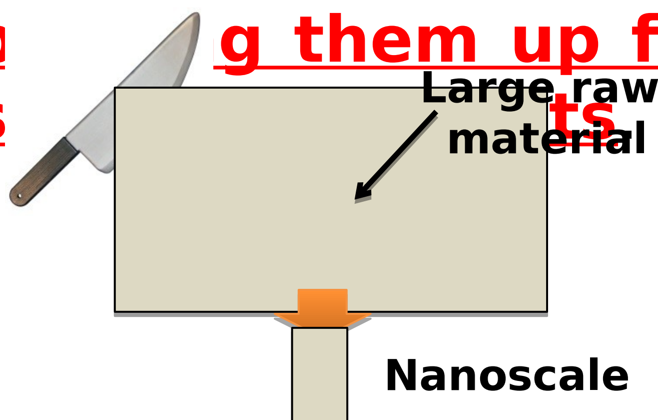
$$\left[\text{Stress} = \frac{F}{A} \quad \text{Strain} = \frac{dL}{L}\right]$$

Stress: force neighboring particles exert on each other
Strain: measure of deformation of material

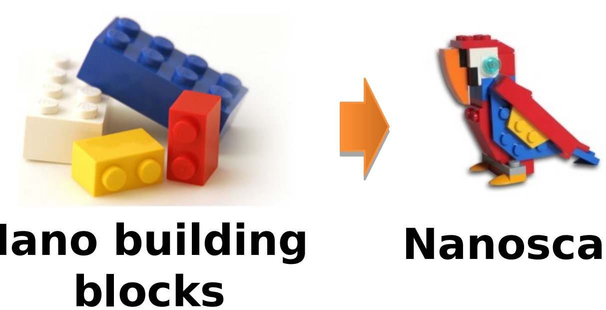
- CNTs have very **large Young's modulus** (~1000 GPa) and **high tensile strength** (~300 GPa).

ynthesizing at Nanoscale

- There are two basic approaches to Nano-manufacturing: **top-down** or **bottom-up**.
- Top-down approach **reduces large pieces of materials down to nanoscale**. This **requires larger amount of materials** and can lead to waste if excess material is discarded.
- Bottom-up approach **creates products by b g them up from atomic- and molecular-s ts**.



Top-down approach



Bottom-up approach

ynthesizing at Nanoscale

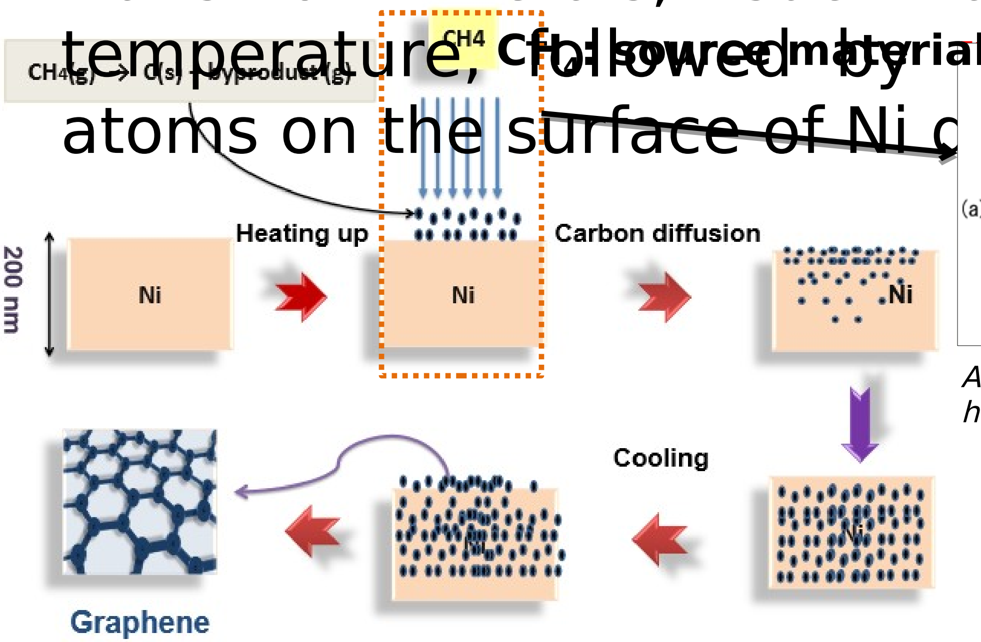
- Bottom-up approach has several **advantages**:
  - Provides **high production rate** and ability to organize the Nano-structures into **desired pattern**.
  - Can integrate **heterogeneous Nano-structures**.
  - Allows precisely controlling the position of Nano-structures, therefore **minimizing generation of defects** in self-assembly.
  - **Cost effective** manufacturing of more complex structures.
- There are more advanced processes of Nano-manufacturing:
  - Chemical Vapor Deposition (CVD).
  - Hydrothermal Synthesis.
  - Arc and Laser Vaporization.

emical Vapor Deposition (CVD)

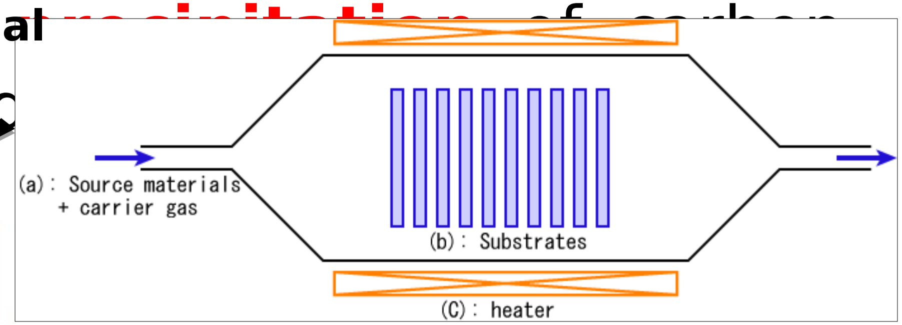
Synthesis of graphene

- This technique involves growing graphene films on different kinds of **substrates with catalyst** (Si/SiO_2/Ni), mainly **transition metals**.

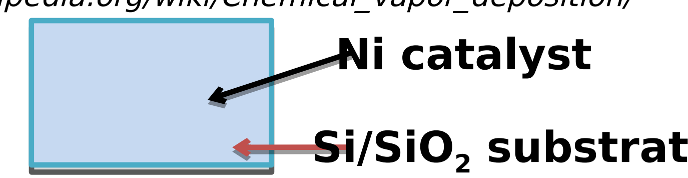
- **Diffusion** of decomposed carbon atoms into transition metals, such as Ni occurs at high temperature, followed by **precipitation** of carbon atoms on the surface of Ni c



Adopted from: http://www.comsol.com/blogs/synthesizing-graphene-chemical-vapor deposition/



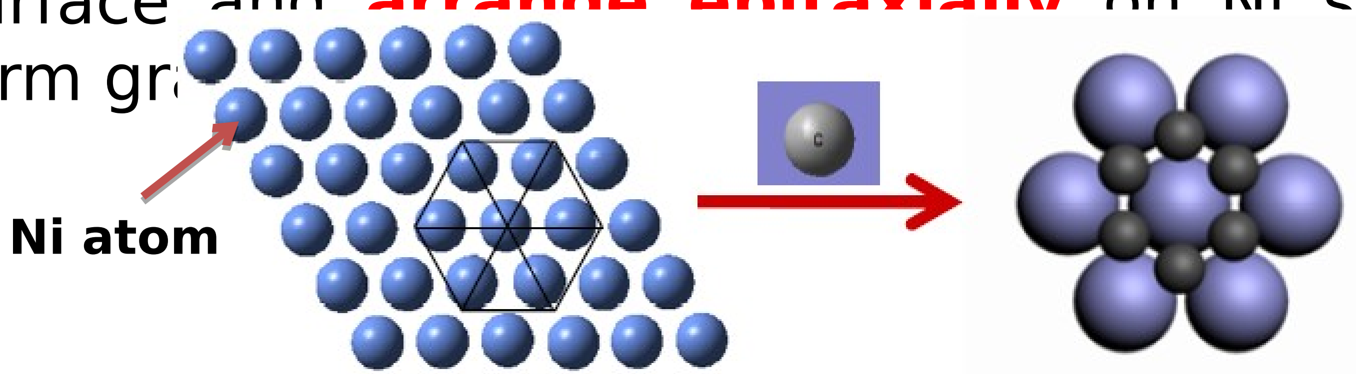
Adopted from: https://en.wikipedia.org/wiki/Chemical_vapor_deposition/



emical Vapor Deposition (CVD)

Synthesis of graphene

- Ni films provide a **good geometrical fit** of ordered graphene to the crystalline metal surface.
- Ni films also provide **good interactions** that **favors bond formation** between carbon atoms at specific conditions.
- Carbon atoms from CH_4 dissolve into Ni crystalline surface and **arrange epitaxially** on Ni surface to form gr



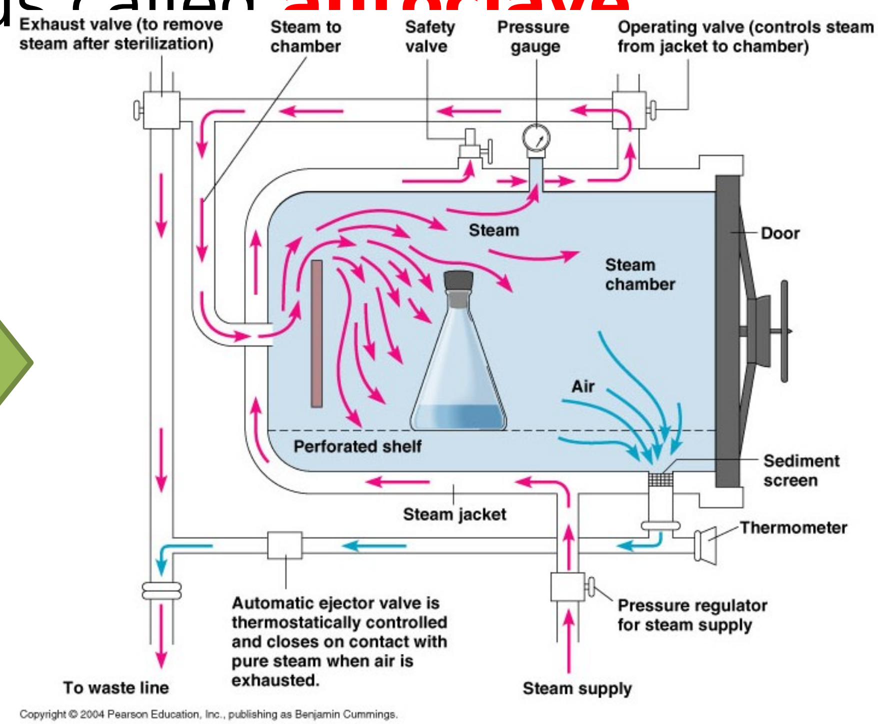
Adopted from: Lewis M.G.D.A., 2010. Dissertation. University of Southern California.

ydrothermal Synthesis

nthesis of Metal-based Nanomaterials

- Hydrothermal synthesis is the technique of crystallizing nanomaterials from **high temperature aqueous solutions** at **high vapor pressure**.
- The growth of nanomaterials, such as metal oxides, is performed in an apparatus called **autoclave**.

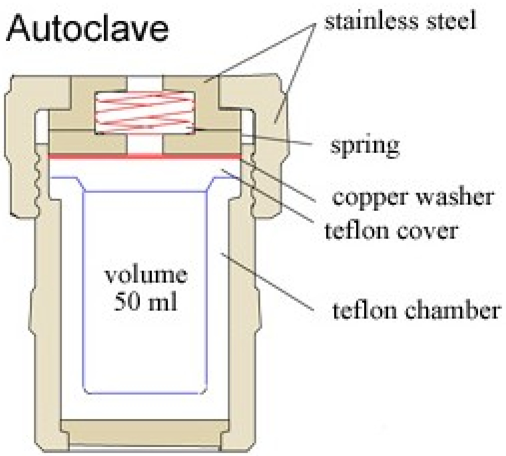
Autoclave



ydrothermal Synthesis

Synthesis of Metal-based Nanomaterials

- Reactants are dissolved in water or other solvent in a **closed vessel**.
- The bomb is heated above boiling point of water to become **supercritical water**.
- An **alkaline solution** is usually added to **increase the solubility**.
- Hydrothermal synthesis is used for oxide nanoparticle since the solubility is high in alkaline medium.



ydrothermal Synthesis

nthesis of Metal-based Nanomaterials

- Advantages of hydrothermal synthesis:
   Simple equipment and **low cost**
   Without the use of catalyst and **less hazardous**
   Large area uniform production
   Very **easy to control the particle size**
- However, hydrothermal synthesis **cannot be applied to all materials**.

plications of Nanotechnology – Medical

Target Nanovectors for Therapy and Diagnosis

- Nanoparticles should be programmed to **locate specific types of cells** (*e.g. tumor cell*) and perform **some actions to kill the cells**.

- Dispensing drugs with the **use of nanoparticle** to provide therapy by heating up in response to external stimulus and killing cell is called **hyperthermia**.

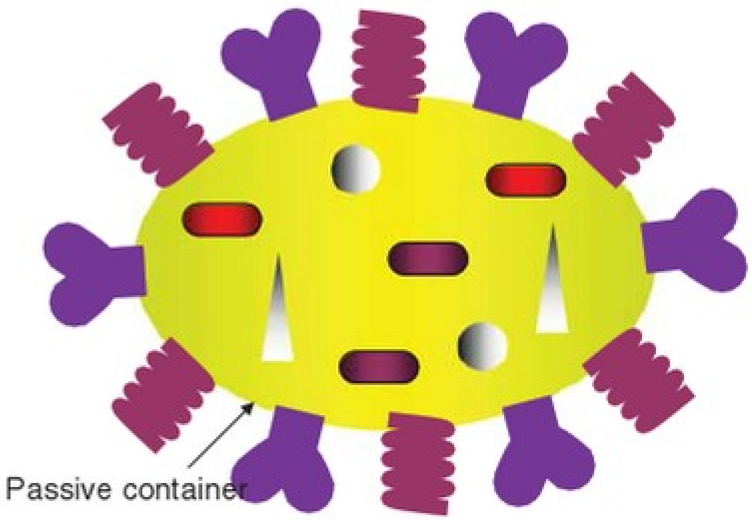
- A **fully functional nanoparticle** programmed to **locate and kill diseased cells** is called **nanovector**.

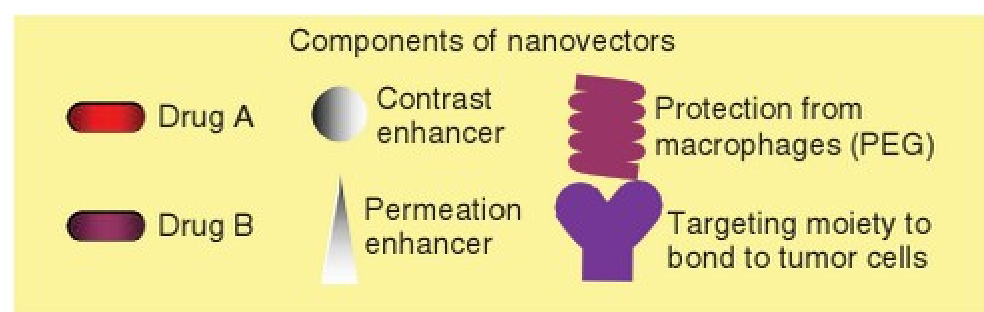
- These are especially useful for **Magnetic**

plications of Nanotechnology – Medical

Types of Nanovectors

a. **Fully functional nanovector** consisting of passive container (~100nm) with ***contrast enhancers for MRI, permeation enhancers*** for passing through blood vessel walls. The particle has ***targeting moieties*** on outside for attaching to diseased cell and ***protection from macrophages (PEG)*** as part of body's passive immune system.

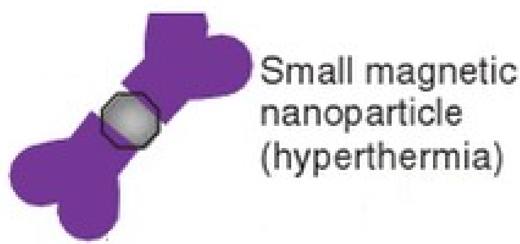


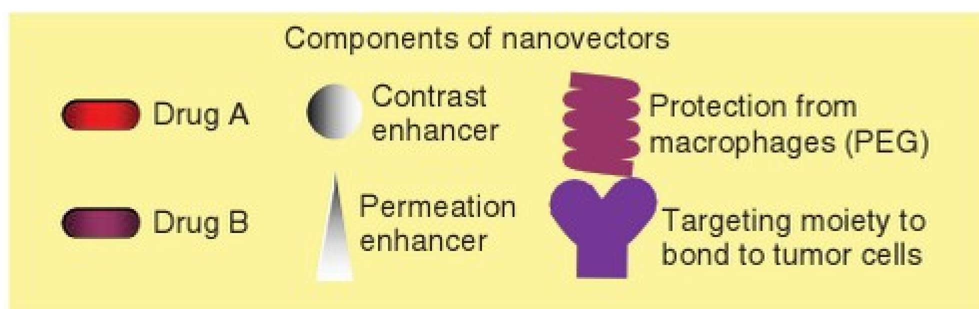


plications of Nanotechnology – Medical

Types of Nanovectors

b. **Simpler nanovector** consisting of small (~10nm) nanoparticle that is targeted to the right type of cell and then **heated by external magnetic field** applied from outside of body. **Large number can produce heat enough to kill the diseased cell**.



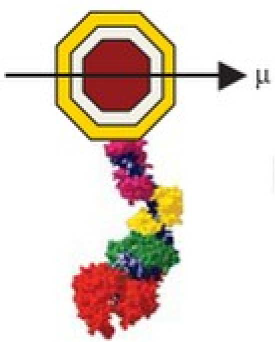


plications of Nanotechnology – Medical

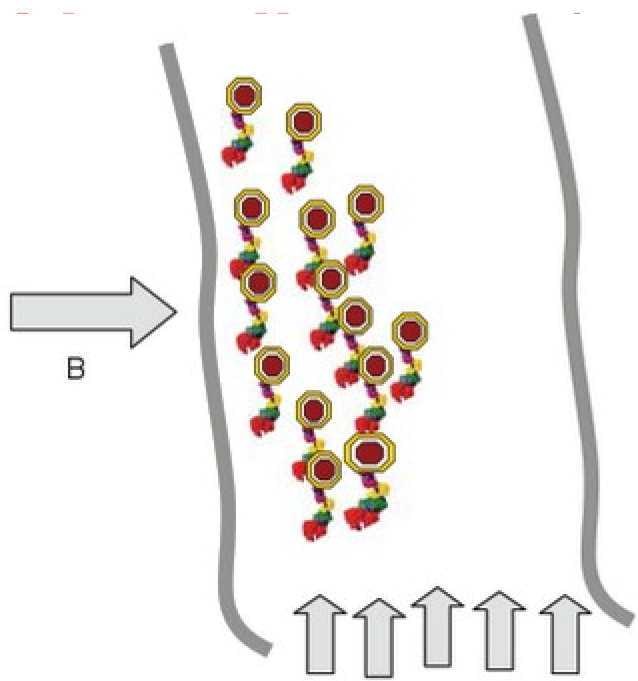
Magnetic Targeting

- **Principle:** To **attach a drug** to **magnetic nanoparticles** that can be **concentrated at the correct site** of diseased cell and **kept there by an external magnetic field**.

- A **magnetic fie** ... es an **attractive force** on a mag



Magnetic carrier nanoparticle

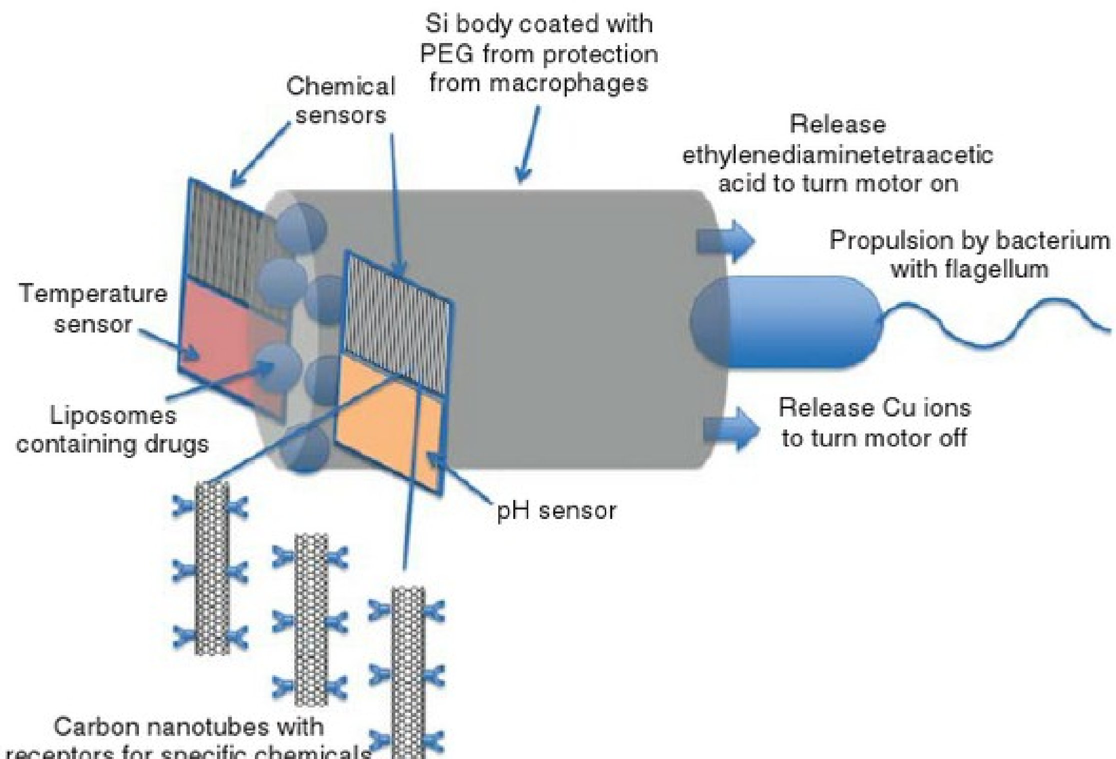


Loaded nanoparticle carriers in a blood vessel **attracted** to an external magnetic field source and **trapped**

plications of Nanotechnology – Medical

Medical Nanobot

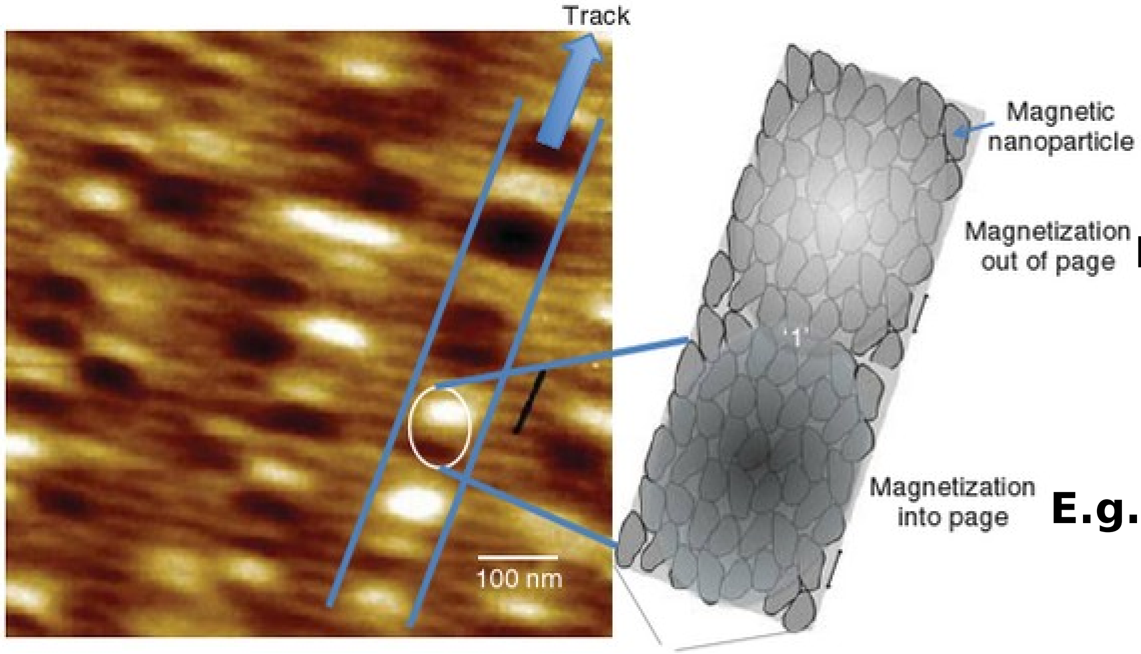
- A machine that is smaller than red blood cell and is **equipped with different detectors**. It can **communicate any findings to outside body** and receive instructions. Attachment of single molecule of chem change in conducti



lications of Nanotechnology – Electronics

Data Storage

- Digital data are stored as a series of **binary digits** or bits (‘1’ or ‘0’).
- Data on hard disks are stored on a **continuous magnetic film** consisting of **densely packed nanop** … on the … **data bits writte** … ing many particle …



E.g. ‘Up’ □ ‘1’

E.g. ‘Down’ □ ‘0’

lications of Nanotechnology – Electronics

Data Storage

- Data could be stored by **magnetizing individual** magnetic nanoparticles such as Fe particle with diameter of 3 nm.
- E.g. ‘Up’ magnetization could represent ‘1’ and ‘Down’ magnetization represents ‘0’. Recording density could reach 100 Tb/in.^{2}.
- ***Advantages***: **Large volume storage** & **data non-volatility**

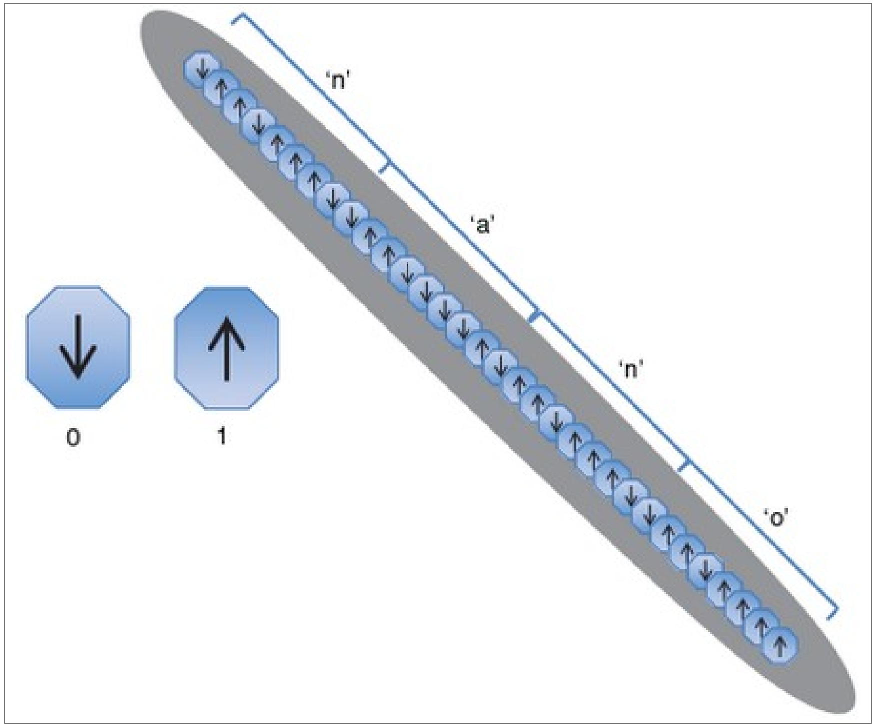


Image shows the word ‘*nano*’ stored in ASCII code along a line of particles